Claims:

1). A hollow fiber membrane made of a perfluorinated thermoplastic comprising a skinned surface on one diameter and a porous surface on the opposite diameter.

2). The membrane of Claim 1 wherein the skinned surface is non-porous.

3). The membrane of Claim 1 wherein the skinned surface is porous with an average pore size range of from about 2 nanometers to about 50 nanometers.

4). The membrane of Claim 1 wherein the membrane is an ultrafiltration membrane.

5). A hollow fiber ultrafiltration membrane made of perfluorinated thermoplastic comprising a skinned surface on one diameter and a porous surface on the opposite diameter capable of retaining macromolecular species dissolved in the class consisting of organic solvents, mixtures of organic solvents, organic solvent/water mixtures, mixtures of organic solvents/water mixtures, and water, wherein the members of the class may have other species dissolved therein.

6). The membrane of Claim 5 wherein the membrane has a molecular weight cutoff of less than 500,000 Daltons.

7). The membrane of Claim 6 wherein the membrane has a molecular weight cutoff of less than 100,000 Daltons.

8). The membrane of Claim 7 wherein the membrane has a molecular weight cutoff of less than 50,000 Daltons.

9). The membrane of Claim 8 wherein the membrane has a molecular weight cutoff of less than 10,000 Daltons.

10). A hollow fiber membrane contactor comprising a hollow fiber membrane made of a perfluorinated thermoplastic comprising a skinned surface on one diameter, and a porous surface on the opposite diameter.

11). The membrane of Claim 10, wherein the skinned surface is non-porous.

12). The membrane of Claim 10, wherein the skinned surface has a porous surface with an average pore size range of from about 2 nanometers to about 50 nanometers.

13). A hollow fiber contactor membrane made of perfluorinated thermoplastic comprising a skinned surface on one diameter and a porous surface on the opposite diameter capable of liquid-gas mass transfer with a Sherwood number equal to about 1.64 times the Graetz number to the 0.33 power in a range of Graetz numbers of from about 5 to about 1000.

14). A hollow fiber contactor membrane made of perfluorinated thermoplastic comprising a skinned surface on one diameter and a porous surface on the opposite diameter capable of liquid-gas mass transfer with liquids having surface tension values of greater than about 20 mN/m.

15). A hollow fiber contactor membrane made of perfluorinated thermoplastic comprising a skinned surface on one diameter and a porous surface on the opposite diameter capable of liquid-gas mass transfer having an intrusion pressure of greater than about 50 psi with isopropyl alcohol.

16). The membrane of Claim 15 having an intrusion pressure of greater than about 10 psi with isopropyl alcohol.

17). The membrane of any one of Claims 1, 5,10, 13, 14 and 15 wherein said perfluorinated thermoplastic polymer is selected from the group consisting of poly(tetrafluoroethylene-co-perfluoro(alkylvinylether)),poly(tetrafluoroethylene-co-hexafluoropropylene), and blends thereof.

18). The membrane of Claim 17 wherein the alkyl of said poly(tetrafluoroethylene-co-perfluoro(alkylvinylether)) is selected from the group consisting of propyl, methyl, and blends of methyl and propyl.

19). A method of producing a hollow fiber membrane from a perfluorinated thermoplastic polymer having a skinned inner surface and a porous structure throughout the remainder of the membrane comprising;

a) dissolving a perfluorinated thermoplastic polymer in a solvent that forms an upper critical solution temperature solution with said polymer,

b) extruding said solution through an annular die, a portion of said die being submerged in a cooling bath, and maintained at a temperature sufficiently high to prevent said solution from prematurely cooling,

c) simultaneously supplying a stream of pressurized fluid to the central portion of the die,

d) extruding said solution into a cooling bath,

e) cooling said solution to below the upper critical solution temperature to cause separation into two phases by liquid-liquid phase separation, said phases being a polymer rich solid phase, and a solvent rich liquid phase, to form a gel fiber,

f) extracting said solvent from said gel fiber to form a hollow fiber membrane having a substantially non-porous inner surface and a substantially porous structure through the remainder of the fiber,

g) drying said porous hollow fiber membrane.

20). The method of Claim 19 wherein said portion of said die being submerged is the die tip and wherein the pressurized fluid is a gas.

21). The method of Claim 19 wherein said perfluorinated thermoplastic polymer is dissolved in a concentration of from about 12% to about 75% by weight in a solvent that forms an upper critical solution temperature solution with said polymer.

22). The method of Claim 19 wherein step (b) comprises extruding said solution in an essentially horizontal attitude through an annular die, said die maintained at a temperature sufficiently high to prevent said solution from prematurely cooling, wherein the tip of said die penetrates through a wall separating said the body of said die from cooling bath, exposing the die exit to said cooling bath liquid.

23). The method of Claim 19 wherein the solvent has a boiling point lower than the temperature of the gel fiber at the die tip exit.

24). The method of Claim 19 wherein the solvent is a low molecular weight saturated chlorotrifluorohydrocarbon polymer.

25). The method of Claim 24 wherein the solvent has a boiling point of less than 290°C.

26). The method of Claim 24 wherein the solvent is selected from the group consisting of HaloVac 60, HaloVac 56 and blends thereof.

27). The method of Claim 19 wherein said perfluorinated thermoplastic polymer is selected from the group consisting of poly(tetrafluoroethylene-co-perfluoro(alkylvinylether)), poly(tetrafluoroethylene-co-hexafluoropropylene) and blends thereof.

28). The method of Claim 27 wherein the polymer is poly(tetrafluoroethylene-co-perfluoro(alkylvinylether)) and the alkyl is selected from the group consisting of propyl, methyl, and blends of methyl and propyl.

29). The method of Claim 19 wherein said cooling bath liquid consists of a non-solvent for said perfluorinated thermoplastic polymer.

30). The method of Claim 19 wherein said cooling bath liquid consists of the group selected from mineral oil, silicone oil or dioctylpthalate.

31). A method of producing a hollow fiber membrane from a perfluorinated thermoplastic polymer having a skinned outer surface and a porous structure throughout the remainder of the membrane comprising;

a) dissolving a perfluorinated thermoplastic polymer in a solvent that forms an upper critical solution temperature solution with said polymer,

b) extruding said solution through an annular die maintained at a temperature sufficiently high to prevent said solution from prematurely cooling,

c) simultaneously supplying a liquid to the lumen of the extrudate through the central portion of the die,

d) extruding said solution into said cooling bath through an air gap with an air contact time of less than about 0.05 second,

e) cooling said solution to below the upper critical solution temperature to cause separation into two phases by liquid-liquid phase separation, said phases being a polymer rich solid phase, and a solvent rich liquid phase, to form a gel fiber,

f) extracting said solvent from said gel fiber to form a hollow fiber membrane having a substantially non-porous inner surface and a substantially porous structure through the remainder of the fiber,

g) drying said porous hollow fiber membrane.

32). The method of Claim 31 wherein the air contact time of step d. is less than about 0.02 second.

33). The method of Claim 31 wherein said perfluorinated thermoplastic polymer is dissolved in a concentration of from about 30% to about 65% by

weight in a solvent that forms an upper critical solution temperature solution with said polymer.

34). The method of Claim 31 wherein step (b) comprises extruding said solution in an essentially horizontal attitude through an annular die, said die maintained at a temperature sufficiently high to prevent said solution from prematurely cooling, wherein the tip of said die penetrates through a wall separating said the body of said die from cooling bath, and wherein the extrudate passes through an air gap before contacting said cooling bath.

35). The method of Claim 31 wherein the solvent has a boiling point lower than the temperature of the gel fiber at the die tip exit.

36). The method of Claim 31 wherein the solvent is a low molecular weight saturated chlorotrifluorohydrocarbon polymer.

37). The method of Claim 31 wherein the solvent is selected from the group consisting of HaloVac 60, HaloVac 56 and blends thereof.

38). The method of Claim 31wherein said perfluorinated thermoplastic polymer is selected from the group consisting of poly(tetrafluoroethylene-co-perfluoro(alkylvinylether)), poly(tetrafluoroethylene-co-hexafluoropropylene) and blends thereof.

39). The method of Claim 31 wherein the polymer is poly(tetrafluoroethylene-co-perfluoro(alkylvinylether)) and the alkyl is selected from the group consisting of propyl, methyl, and blends of methyl and propyl.

40). The method of Claim 31wherein said cooling bath liquid consists of a non-solvent for said perfluorinated thermoplastic polymer.

41). The method of Claim 31 wherein said cooling bath liquid is selected from the group consisting of mineral oil, silicone oil and dioctylpthalate.

42). The method of Claim 31 wherein said liquid supplied to the lumen cis selected from the group consisting of a low molecular weight saturated chlorotrifluorohydrocarbon polymer, mineral oil, silicone oil, and dioctylpthalate.

43). A hollow fiber membrane made of a perfluorinated thermoplastic comprising a skinned surface on one diameter, a porous surface on the opposite diameter, produced by the method of any one of the Claims 18 and 31.

44). The membrane of Claim 43 wherein said perfluorinated thermoplastic polymer is selected from the group consisting of poly(tetrafluoroethylene-co-perfluoro(alkylvinylether)), poly(tetrafluoroethylene-co-hexafluoropropylene), and blends thereof.

45). The membrane of Claim 43, wherein the alkyl of said poly(tetrafluoroethylene-co-perfluoro(alkylvinylether)) is selected from the group consisting of essentially all propyl, of essentially all methyl, and blends of methyl and propyl.

46). The membrane of Claim 43 wherein the skinned surface is non-porous.

47). The membrane of Claim 43 wherein the membrane has a porous surface with an average pore size range of from about 2 nanometers to about 50 nanometers.